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# Time correlation function and finite field approaches to the calculation of the fifth order Raman response in liquid xenon

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# Time correlation function and finite field approaches to the calculation of the fifth order Raman response in liquid xenon

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The fifth order, two-dimensional Raman response in liquid xenon is calculated via a time correlation function (TCF) theory and the numerically exact finite field method. Both employ classical molecular dynamics simulations. The results are shown to be in excellent agreement, suggesting the efficacy of the TCF approach, in which the response function is written approximately in terms of a single classical multitime TCF. © 2006 American Institute of Physics. [DOI: [10.1063/1.2403129](https://doi.org/10.1063/1.2403129)]

The desire to further probe the complex structural and dynamical information present even in simple liquids has lead to the recent development of sophisticated experimental spectroscopic techniques. One such technique, fifth order Raman spectroscopy [referred to here as two-dimensional (2D) Raman spectroscopy], was suggested as effective in assessing structural and dynamical contributions to spectral line shapes, e.g., it can distinguish between the limiting cases of homogeneous and inhomogeneous broadening.<sup>1</sup> However, from an experimental point of view, the technique presents a challenge created by weak signal strength and interference from lower order signals, i.e., third order cascades.<sup>2–9</sup> Furthermore, the signals attained are very difficult to interpret; thus numerically demanding theoretical approaches have been pursued by many researchers.<sup>1,10–25</sup>

One such theoretical approach is a computationally tractable two-time classical time correlation function (TCF) theory for the quantum response function.<sup>10,22,26,27</sup> The relative simplicity of the theory, writing the response function in terms of a single classical multitime TCF, also offers the possibility of gaining insight into what physical phenomena are usefully probed by 2D Raman experiments. It should be noted, however, that little theory exists on the nature of multitime TCF at this point.<sup>28</sup> Of course, the theory is only useful if it is effective. Here we will demonstrate that even the 2D Raman spectrum of a simple Lennard-Jones liquid exhibits a sharp dependence on polarization condition, and that our TCF theory captures these distinct line shapes as demonstrated by comparison with numerically exact finite field (FF) calculations.

An analogous approach was applied to the third order dipole response that is responsible for two-dimensional infrared spectra, and the success here suggests that the theory might also be quite effective. In the case of two-dimensional infrared spectroscopy, exact calculations are not possible, even in the classical limit, making a TCF theory an attractive option.<sup>29</sup>

Although multidimensional nonlinear spectra cannot be expressed exactly in terms of classical TCF,<sup>21</sup> the TCF approach was first shown to be effective by comparison with the only exact classical calculation available at the time. However, those calculations were done using approximations for the polarizability that made them physically less relevant, and only the fully polarized spectrum<sup>10,19</sup> was considered. In the classical limit, appropriate for low frequency intermolecular spectra, the TCF method essentially provides an approximation to the Poisson bracket calculation that otherwise requires the extremely demanding calculation of the stability matrix. Another more tractable numerically exact method for calculating 2D Raman spectra has recently been proposed.<sup>23,24,30</sup>

The FF molecular dynamics (MD) method aims to simulate the actual experiment by applying a finite field to the molecular system which represents the interaction of the system with the electric field in the experiment;<sup>14,31</sup> there is no need to calculate the stability matrix.<sup>14</sup> In this paper, results from the FF and TCF approaches are directly compared serving to help further validate the TCF theory. Details of the TCF theory and the FF method are provided elsewhere.<sup>14,22,31</sup>

The quantum mechanical expression for the electronically nonresonant fifth order polarization response is given by<sup>1,32</sup>

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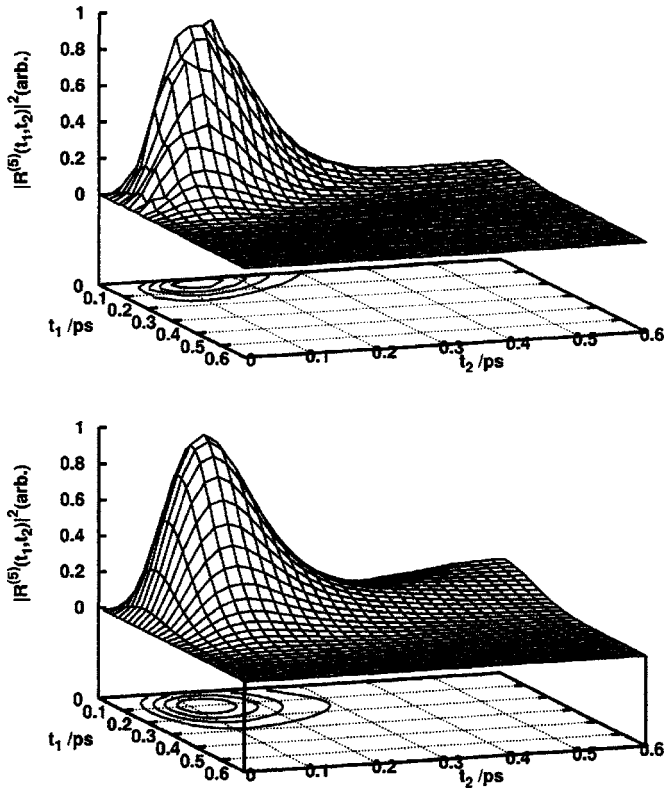


FIG. 1. Shown here is the fully polarized fifth order response function,  $R_{xxxxx}^{(5)}(t_1, t_2)$ , for the temperature  $T^* = 1.0$  (222 K) from the TCF method (top) and the FF method (lower).

$$R_{\alpha\beta\gamma\delta\epsilon\phi}^{(5)}(t_1, t_2) (i/\hbar)^2 \text{Tr}\{\Pi^{\alpha\beta}(t_1 + t_2) [\Pi^{\gamma\delta}(t_1), [\Pi^{\epsilon\phi}(0), \rho]]\}. \quad (1)$$

In Eq. (1),  $\rho = e^{-\beta\Pi}/Q$ , for a system with Hamiltonian  $H$  and partition function  $Q$  at reciprocal temperature  $\beta = 1/kT$ , and  $k$  is Boltzmann's constant;  $\text{Tr}$  represents a trace, square brackets denote commutators,  $\Pi$  is the system polarizability tensor, and the Greek superscripts denote the elements and thus polarization condition being considered. The classical limit of the trace is of order  $\hbar^2$  and results from a combination of four two-time correlation functions that are themselves equivalent classically.<sup>22</sup> Alternatively the commutators can be replaced by Poisson brackets to achieve a different form of the classical limit as is done in the stability matrix approach.

For the calculations presented here, MD simulations were performed for a neat liquid xenon system consisting of 108 atoms at a density of  $\rho\sigma^3 = 0.8$ . The atoms interacted via a Lennard-Jones pair potential with  $\sigma = 4.099$  Å and  $\epsilon = 222$  K. Polarization forces were not explicitly included in the MD simulations; however, full many body polarization effects were included in the polarizability calculations used in the TCF and FF methods via a point atomic polarizability approximation.<sup>33,34</sup> The effective polarizability  $\tilde{\alpha}_i$  for site (atom)  $i$  is given by

$$\tilde{\alpha}_i = \alpha_i + \alpha_i \sum_{j \neq i}^n T(\mathbf{r}_{ij}) \cdot \tilde{\alpha}_j, \quad (2)$$

where  $\alpha_i$  is the isotropic point polarizability for site  $i$  and  $T(\mathbf{r}_{ij})$  is the dipole tensor. The total system polarizability is

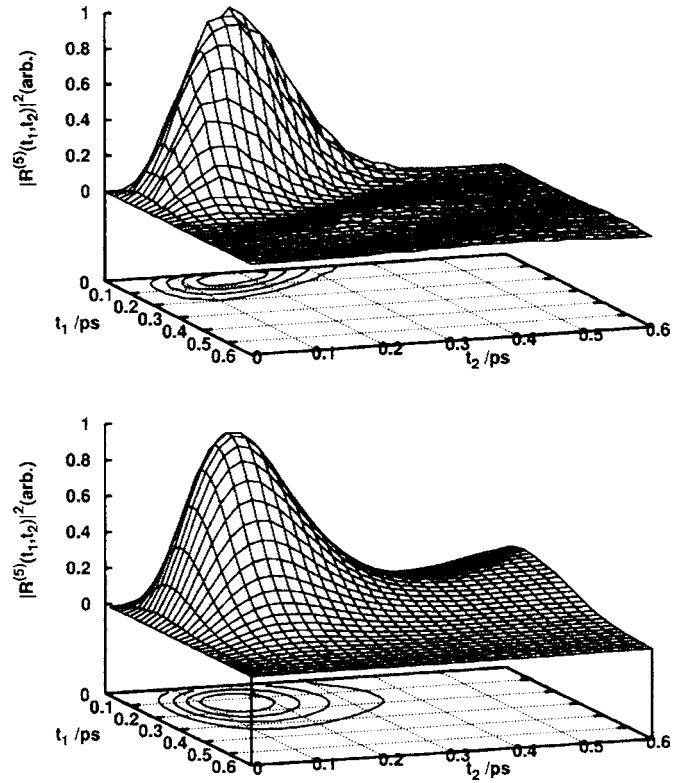


FIG. 2. This figure presents the fully polarized fifth order response function,  $R_{xxxxx}^{(5)}(t_1, t_2)$ , for the temperature  $T^* = 0.5$  (111 K) by employing the TCF method (top) and the FF method (lower).

given by summing the effective polarizabilities for all sites,

$$\Pi = \sum_{i=1}^n \tilde{\alpha}_i. \quad (3)$$

An exact, matrix inversion based, solution of Eq. (2) was used for the present calculations.

Calculated the fifth order Raman response functions  $R^{(5)}(t_1, t_2)$  using the two above mentioned methods are found to be in excellent agreement, while the spectra vary greatly depending on the polarization condition. In all the following, the TCF and FF results are shown in the upper and lower panels of the figures, respectively. All of the results presented here have been normalized to unity. The fully polarized,  $xxxxx$  response,  $R_{xxxxx}^{(5)}(t_1, t_2)$ , is shown in Fig. 1 for the reduced temperature,  $T^* = 1.0$ . The TCF calculation constitutes a prediction of the experimental or simulation result, and is quite different from an earlier calculation employing a first order dipole induced dipole approximation<sup>10,19,27</sup> for the polarizability. Both methods predict a single peak along  $t_2$  with the maximum occurring at  $t_2 \approx 125$  fs with similar decay times along both axes. The temperature dependence of the fully polarized response is illustrated in Figs. 2 and 3 for the reduced temperatures,  $T^* = 0.5$  and  $2.0$ , respectively. These figures also indicate the nearly quantitative agreement attained by the two methods. Figure 2 again shows a single peak along  $t_2$  with the maximum occurring at  $t_2 \approx 150$  fs with similar rise and decay times for both methods. Finally, Fig. 3 shows a single peak with the maximum occurring at  $t_2 \approx 100$  fs with similar rise and decay times as well. The

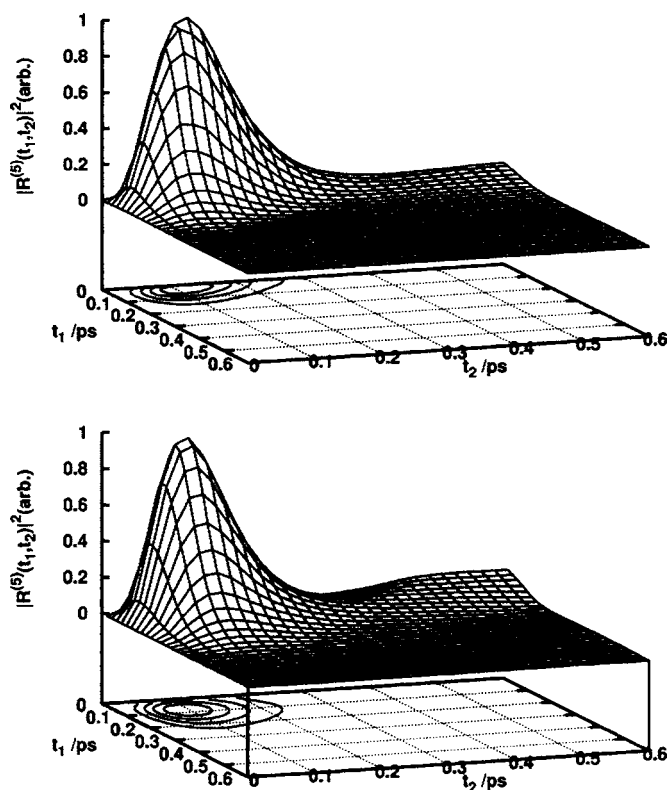


FIG. 3. This figure presents the fully polarized fifth order response function,  $R^{(5)}_{xxxxx}(t_1, t_2)$ , for the temperature  $T^* = 2.0$  (444 K) by employing the TCF method (top) and the FF method (lower).

minor difference between the two methods is that the TCF method predicts shorter rise times (almost instantaneously) in the  $t_1$  direction, whereas the FF method predicts the peak maximums at  $t_1 \approx 100$  fs.

The results for the semipolarized response function,  $R^{(5)}_{xxxxx}(t_1, t_2)$ , are shown in Fig. 4 for the reduced temperature,  $T^* = 1.0$ . Both methods again predict a single peak with similar rise times in the  $t_1$  direction with the maximum occurring at  $t_2 \approx 100$  fs; however, although both methods predict similar decay times along  $t_2$  initially, the FF method does not completely decay to zero and shows an increase in magnitude beginning at  $t_2 \approx 400$  fs. In contrast, the TCF method decays to zero by  $t_2 \approx 300$  fs and remains zero for the time scales shown here. Again, the FF method predicts slower rise times along  $t_1$  and similar decay times although the FF is shifted to longer times as a result of the slower rise.

A different semipolarized response function,  $R^{(5)}_{xxzxxx}(t_1, t_2)$ , is shown in Fig. 5 for the reduced temperature,  $T^* = 1.0$ . The polarization condition  $xxzxxx$  shows the least agreement between the two methods; however, it is interesting that the major signatures of the spectrum are captured in both methods including the large peak in the center of the plot. This polarization condition was expected to be the most efficient at indicating the relative amount of homogeneous and inhomogeneous broadening present in the system.<sup>13</sup> Both methods predict a small peak along the  $t_2$  axis occurring at  $t_2 \approx 120$  fs, although the TCF method predicts a higher magnitude than the FF method. The spectra from both methods are dominated by a peak with maximum at  $t_1 \approx 200$  fs and

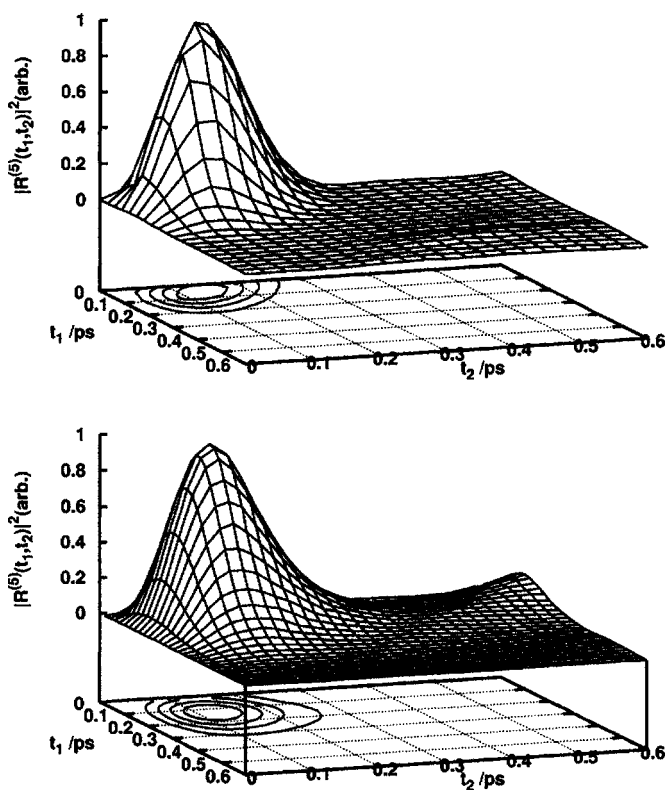


FIG. 4. The semipolarized fifth order response function,  $R^{(5)}_{xxxxx}(t_1, t_2)$ , for the temperature  $T^* = 1.0$  (222 K) is shown from the TCF method (top) and the FF method (lower).

$t_2 \approx 300$  fs with this being shifted to slightly longer times with the FF method compared to the TCF method. The major disagreement between the two methods for this polarization condition is the much slower decay times along both  $t_1$  and  $t_2$  predicted by the FF method.

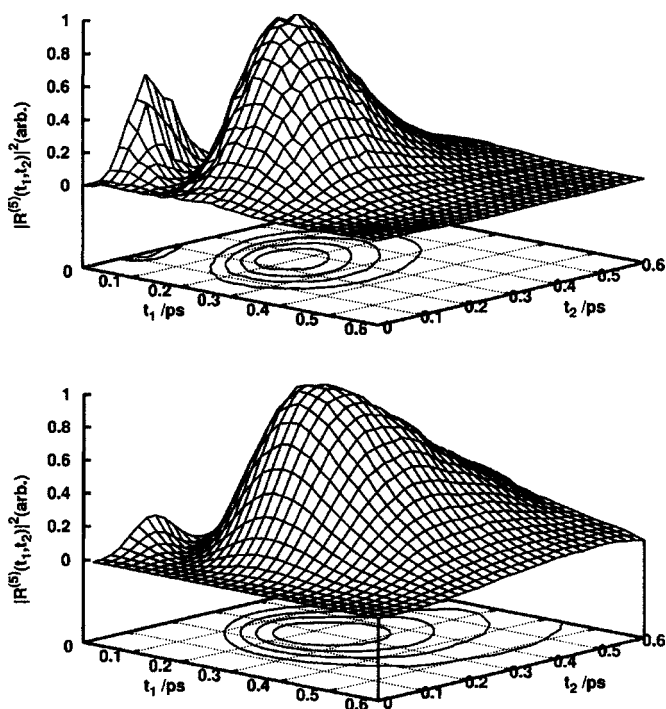


FIG. 5. The semipolarized fifth order response function,  $R^{(5)}_{xxzxxx}(t_1, t_2)$ , for the temperature  $T^* = 1.0$  (222 K) is shown here from the TCF method (top) and the FF method (lower).



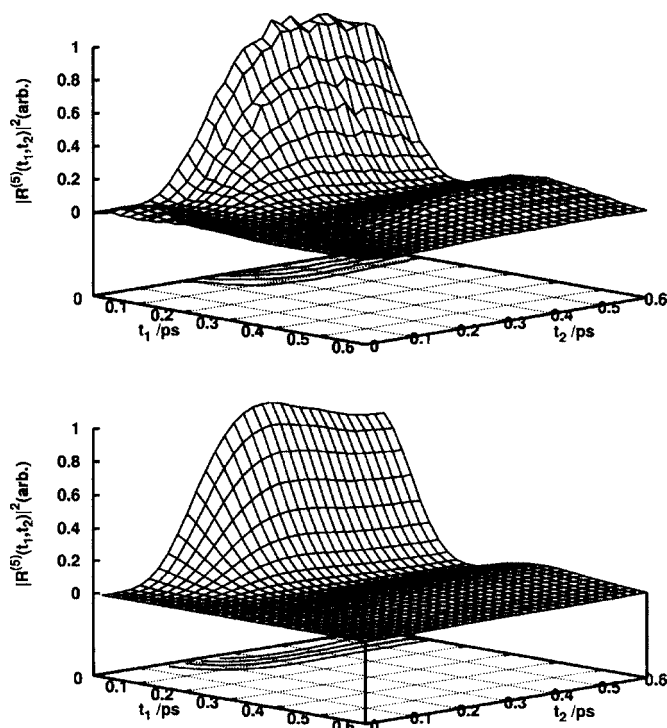


FIG. 6. The semipolarized fifth order response function,  $R_{xxxxx}^{(5)}(t_1, t_2)$ , for the temperature  $T^* = 1.0$  (222 K) is shown here from the TCF method (top) and the FF method (lower).

A third semipolarized response function,  $R_{zzxxx}^{(5)}(t_1, t_2)$ , is shown in Fig. 6 for the reduced temperature,  $T^* = 1.0$ . Both methods predict a ridge along the  $t_2$  axis which extends beyond the time scales shown here. In addition, both methods predict similar rise times along  $t_2$  with the maximum being reached by  $t_2 \approx 360$  fs, and decay times along  $t_1$  with the signal decaying to zero by  $t_1 \approx 200$  fs. Finally, both methods also predict a second small ridge along  $t_2$  at  $t_1 \approx 350$  fs.

Figure 7 shows the depolarized response function,  $R_{zzzzx}^{(5)}(t_1, t_2)$ , for the reduced temperature,  $T^* = 1.0$ . Both methods again capture the signature components of the spectrum including the peak around 150 fs and the slowly decaying ridge along  $t_2$ . The TCF and FF methods predict similar rise times in the  $t_2$  direction, although the FF method predicts slower decay times in the  $t_1$  direction. In addition, the FF method predicts a minimum along  $t_2 = 0$  at  $t_1 \approx 380$  fs followed by an increase in magnitude that extends beyond the time scales shown here. The TCF method suggests a slight increase in magnitude along  $t_2 = 0$ , following the minimum but is much less pronounced with the minimum occurring much later at  $t_2 \approx 500$  fs.

These results suggest the effectiveness of the TCF approach and prompt further attention into the connection between the approximations made in the TCF method and both equilibrium and nonequilibrium exact calculations.

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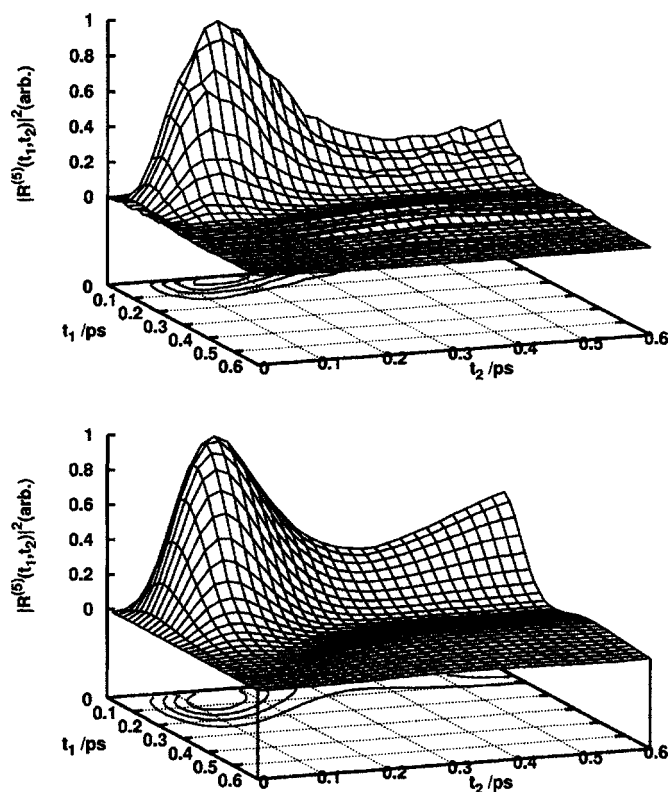


FIG. 7. The depolarized fifth order response function,  $R_{zzzzx}^{(5)}(t_1, t_2)$ , for the temperature  $T^* = 1.0$  (222 K) is shown here from the TCF method (top) and the FF method (lower).

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